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Electron Microscopy Study of TiO_2 Nanoparticle in Mesoporous Silica

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The hybridization of the titanium dioxide (Titania, TiO_2) nanoparticle with mesoporous silicas (MPSs) has been widely investigated for various applications in photocatalysis. The size and the shape of the TiO_2 nanoparticle, as well as their location and spatial distribution in and/or on MPSs are important for the performance of the resulting hybrids through the selectivity, the adsorption of the reactants and the desorption of the products. In addition, the porous structure of MPSs plays an important role as a template to control the size and the shape of TiO_2 nanoparticles. However, the morphology and the location of the TiO_2 nanoparticles in and/or on MPSs were not fully understood [1]. This paper presents the first in-depth study of the relationship between titania nanoparticles and mesoporous silica (MPS, SBA-15) by electron microscopy and other analytical techniques.

Titania nanoparticles were immobilized preferentially into the 8 nm diameter pores of a mesoporous silica, SBA-15, by the impregnation of tetraisopropyl orthotitanate (TTIP) as a TiO_2 precursor [2]. The size of TiO_2 particles was controlled by varying the titania loading, which was achieved by diluting TTIP with isopropanol. The size of TiO_2 particles was derived from XRD, and UV-Vis. absorption spectra. The distribution of the titania particles on the external surface of SBA-15 particles was confirmed by SEM and zeta potential measurement. The remaining porosity of the SBA-15-titania hybrids was characterized by N_2 adsorption/desorption isotherms and was correlated with the titania content to confirm the location of the titania in the pore. The morphology TiO_2 nanoparticles and MPSs were examined in SEM and TEM. To further investigate the distribution of TiO2 in/on MPSs, cross-sectional samples were prepared by FIB, and examined in JEOL 2100 FEG TEM/STEM equipped Oxford EDS and Gatan EELS/GIF systems.

SEM micrograph showed a bundle of cylindrical-shaped particles of TiO2/MPS (SBA-15) retained after the immobilization of TiO_2 (Fig. 1a). The intensity of the diffraction peaks owning to SBA-15 decreased significantly. The shape of the N_2 adsorption isotherm changed from the steep adsorption due to the mesoporous structure of SBA-15 to the broad adsorption from pore filling of the TiO_2 nanoparticles (Figs. 1b and 1c). Micropores can be found in samples prepared by conventional method despite it often formed aggregates and specimen thickness may not be ideal (Fig. 2). Electron diffraction (eD) and elemental analyses reveal TiO_2 nanoparticles were distributed in/on the MPS. However, the exact location of TiO2 is uncertain due to the orientation of samples. To overcome the problem, cross-sectional samples of SBA-15-TiO_2 particles prepared by FIB and ultramicrotome depict TiO_2 nanoparticles filling pores/channels in SBA-15 MPS (Figs. 3 and 4). Electron diffraction and elemental analysis by EDS and EELS confirmed those observed nanoparticles were anatase (TiO_2). The particles size of TiO_2 nanoparticles observed in TEM (8 nm) was consistent with XRD results. The hexagonal arrangement of the 8 nm pore and long channels of SBA-15 inhomogeneously or partially filled by titania were clearly shown in TEM images of TiO_2/MPS particles prepared by FIB and ultramicrotome. The observed pore space was consistent with the remaining porosity of the SBA-15-TiO_2 (283 m^2/g and 0.26 cm^3/g) derived from the N_2 adsorption isotherm [3].

References:

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[3] This work was supported by Res. Chair Grant 2017 (to MO), NSTDA, Thailand, VISTEC scholarship (KV), and by NanoCenter, UMD. Drs. SC Liou and JC Rao provided technical assistance.

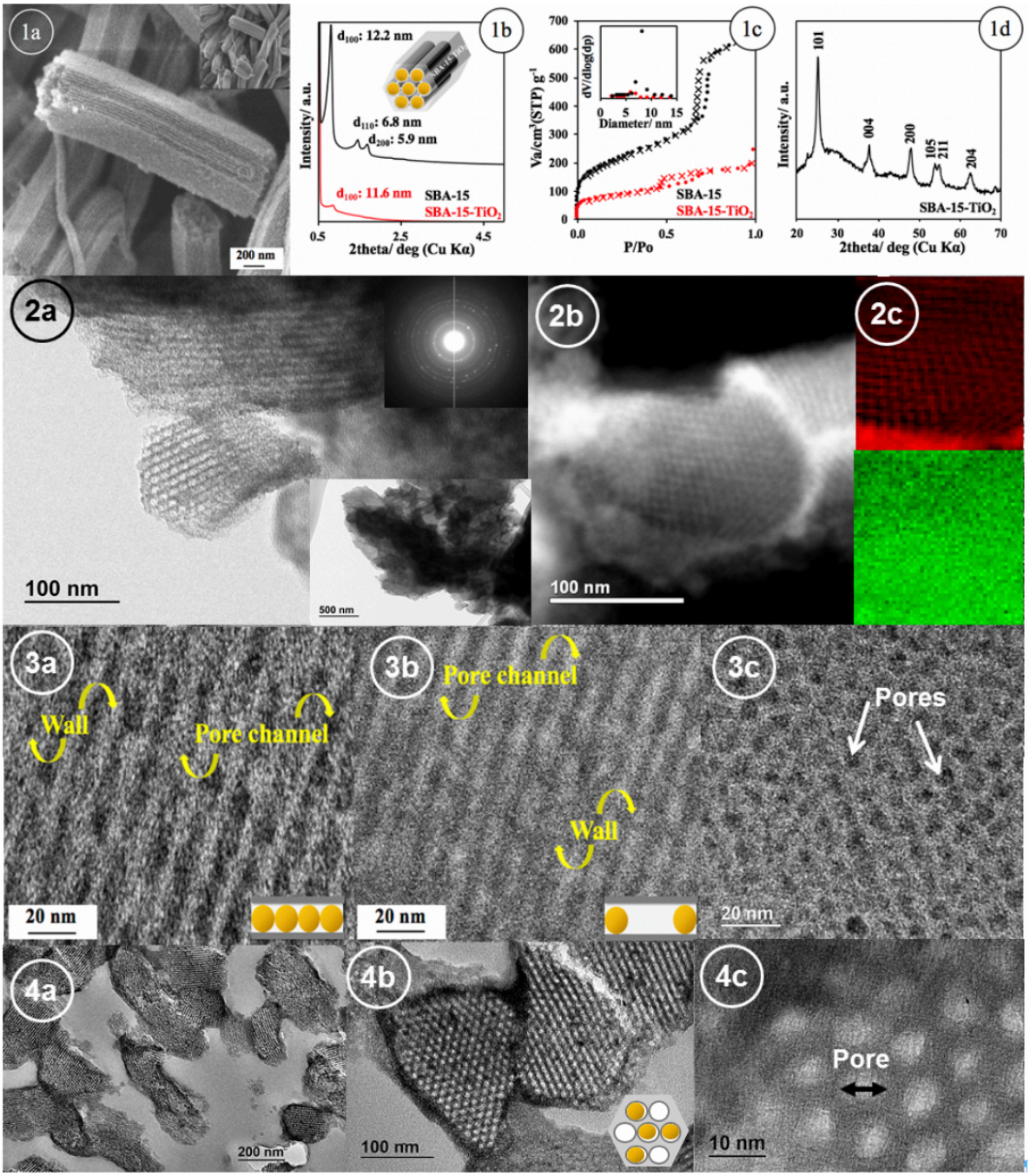

Figure 1. SEM image and wide-angle X-ray diffraction pattern of of SBA-15-TiO_2 (a and c), Low-angle X-ray diffraction patterns and N_2 adsorption/ desorption isotherms of SBA-15 and SBA-15-TiO_2 (b and d)
Figure 2. TEM images and SDA pattern of SBA-15-TiO_2 (a and b). STEM HAAD image and EELS analysis illustrates TiO2 nanoparticles filled pores in MSP.
Figure 3. Cross-sectional TEM images of SBA-15-TiO_2 prepared by FIB shows the distribution of TiO_2 in the pore channel of MPS.
Figure 4. Cross-sectional TEM images of SBA-15-TiO_2 prepared by ultramicrotome depicts the spacial distribution of TiO_2 in MPS.

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